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COLORADO UNIV BOULDER DEPT OF CHEMISTRY
INFRARED CHEMILUMINESCENCE STUDIES OF ION-MOLECULE REACTIONS IN--ETC(U)
MAR 79 S R LEONE, G B ELLISON, V M BIERBAUM AFOSR-78-3565

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER AFOSR-TR-79-0727	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Infrared Chemiluminescence Studies of Ion-Molecule Reactions in a Flowing Afterglow		5. TYPE OF REPORT & PERIOD COVERED Interim April 1, 1978-March 31, 1979	
7. AUTHOR(s) Stephen R./Leone, G. Barney/Ellison Veronica M./Bierbaum		8. CONTRACT OR GRANT NUMBER(s) AFOSR-78-3565	
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Joint Institute for Laboratory Astrophysics and The Department of Chemistry, University of Colorado, Boulder, Colorado 80309		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303/B1	
11. CONTROLLING OFFICE NAME AND ADDRESS AF Office of Scientific Research/NC Building 410 Bolling AFB, D.C. 20332		12. REPORT DATE March 1979	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Interim technical rept. 1 Apr 78-31 Mar 79		13. NUMBER OF PAGES 14	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		15. SECURITY CLASS. (of this report) Unclassified	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Infrared Chemiluminescence Ion-Molecule Reactions Flowing Afterglow			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A flowing afterglow apparatus for infrared chemiluminescence studies of ion-molecule reactions has been successfully constructed, made operational, and two key new experiments completed in the first year of this grant. (continued, over)			

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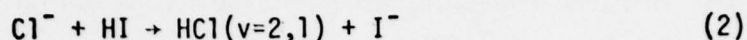
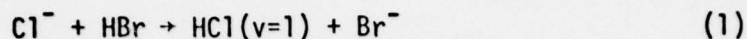
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The kinetics and infrared chemiluminescence of the proton abstraction reactions



have been studied. The rate constant for reaction (1) was measured to be $7.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and bromide ion was determined to be the only ionic product. Infrared emission from vibrationally excited HCl was observed at 3.5μ with the precise frequency and shape of the ion modulation. The emission intensity is directly proportional to chloride ion density, exhibits the proper dependence on HBr concentration and is completely blocked by an HCl gaseous filter, confirming that only $v=1$ is populated.

For reaction (2) the rate constant was determined to be $4.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and iodide was confirmed to be the only ionic product. The distribution of $v=2/v=1$ in HCl was determined to be 0.26/0.74. Both results indicate close similarity to the high levels of vibrational excitation and distributions observed in analogous neutral atom abstraction reactions.

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Interim Technical Report

1 April 1978-31 March 1979


AFOSR Grant # 78-3565

**Title: Infrared chemiluminescence studies of ion-molecule
reactions in a flowing afterglow**

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Veronica M. Bierbaum**

**Institution: University of Colorado
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A flowing afterglow apparatus for infrared chemiluminescence studies of ion-molecule reactions has been successfully constructed, made operational, and two key new experiments completed in the first year of this grant. Figure 1 illustrates the major components of this device. The apparatus consists of a gas handling system, a stainless steel flow tube in which ion production and reaction occur, an infrared detection system with signal averaging equipment for monitoring vibrational chemiluminescence, a quadrupole mass filter for analysis and detection of the ionic species, and a 1600 CFM Roots blower backed by a mechanical pump for maintaining the large gas flow velocities.

In a typical experiment, purified helium buffer gas (0.3 torr) is pumped at high velocity (80 m/sec) through the flow tube and serves to define the fluid dynamics and diffusion properties of the system. Small flows of other gases (e.g., CCl_4 to generate Cl^-) are also added at the upstream end where ionization is effected by electron impact in the ionizer assembly. The resulting plasma flows about 20 cm before introduction of the neutral reactant to allow development of a laminar profile, to bring the ions to thermal equilibrium and to attenuate higher diffusion modes. The neutral reactant (e.g., HBr) is added through the radial inlets or movable inlet ports. At the end of the reaction region, most of the reaction mixture is exhausted through the large Roots pumping system. A fraction of the plasma is sampled through a small orifice in a molybdenum cone, the ions are separated by a quadrupole mass filter and detected with a Ceratron electron multiplier. By appropriate choice of the sign of the applied voltages in the

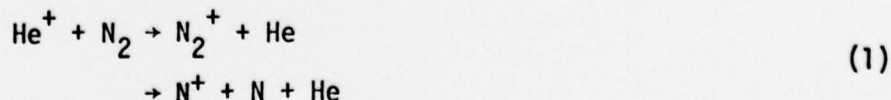
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detection system, either positive or negative ions may be sampled, analyzed and detected. Kinetic data are obtained, as with a conventional flowing afterglow system, by monitoring the total ion spectrum as a function of experimental parameters.

For detection of infrared chemiluminescence, a set of guard rings or a mesh grid are employed in the upstream section of the flow tube to provide a pulsed field region for separation of the ions from radical and metastable species. The neutral reactant is added downstream of this ion separation region and infrared emission is observed through port windows and appropriate filters by a large area InSb or Ge:Cu detector. To date all experiments have been performed with the indium antimonide detector. The copper-doped germanium detector will be housed in a liquid helium cryostat which incorporates field of view apertures and cooled circular variable filters for background reduction and for scanning of infrared emission spectra. The output of these detectors is digitized and signal-averaged for complete time development signals, or alternatively is sampled with a lock-in amplifier for maximum detection of weak signals. The lock-in signal is recorded in the multichannel averager as a function of circular variable filter position to obtain spectra.

This device has all the capabilities of a conventional flowing afterglow. After initial calibrations and tests for leak-tightness and proper operation, the accuracy of the system for quantitative kinetic measurements was examined. The rate constant for the reaction

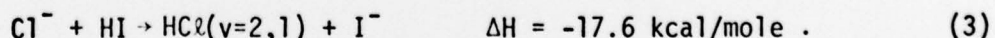
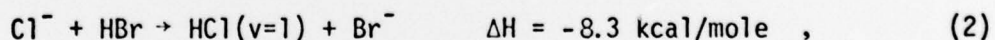


was determined under a variety of experimental conditions and the resulting value ($1.4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is in very good agreement with those

from other laboratories. These experiments also established that the radial inlets provided perfectly uniform gas addition since the end correction was determined to be zero.

Proper operation of the ion separation region is essential for distinguishing between infrared emission from the products of ion-molecule processes and emission arising from neutral reactions or excited species. A variety of experiments was performed to determine the best conditions for ion separation and several general conclusions were reached: 1) The lowest voltage (~ 10 -15 V) which effects 100% ion modulation should be employed. Higher potentials cause collisional detachment of negative ions to generate electrons and radicals. The enhanced radical concentration and subsequent reactions can seriously obscure the ion signals. 2) Asymmetrical square waves, in which ions are transmitted for 95% of the cycle, are most effective. This minimizes ion "pile-up" and allows use of low voltages. 3) Modulation frequencies of about 50 Hz are optimum. At higher frequencies axial diffusion mixes the ion pulses while lower frequencies unnecessarily lengthens the data acquisition time. 4) Under comparable conditions, the mesh grid always provided more complete ion modulation than did the guard rings.

Our first detailed study of infrared chemiluminescence has been the gas phase proton abstraction reactions



These reactions were chosen for a variety of reasons. The generation of copious amounts of chloride ions is straightforward. The neutral reactants are commercially available, stable compounds. The reaction rates, although previously not measured, were expected to be rapid, and a single reaction

pathway is predicted. Moreover the infrared spectrum of HCl has been well characterized and the necessary data can be obtained with the InSb detector. Finally, these reactions provide a very important data base for comparison to analogous neutral reaction processes used in chemical lasers.

Cl⁻ + HBr

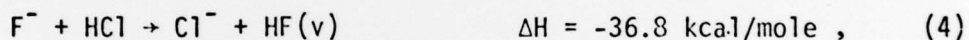
The reaction rate constant was measured to be $k = 7.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Figure 2) and bromide ion was determined to be the only ionic product. Infrared emission from vibrationally excited HCl was observed at 3.5μ , with the precise frequency and shape of the ion modulation (Figure 3). The time interval between the infrared emission signal and the detected ion signal exactly reflects the ion flow time from the infrared port window to the mass spectrometer. The HCl infrared emission intensity is directly proportional to chloride ion density and exhibits proper dependence on hydrogen bromide concentration (Figure 4). In Figure 4 the infrared emission increases with HBr addition until complete reaction of chloride ion is achieved; beyond this endpoint of maximum production of hydrogen chloride, no further increase in chemiluminescence is seen. Upon introduction of an HCl gaseous filter, all emission was blocked confirming that only $v=1$ had been populated. This result is consistent with predictions based on the exothermicity of the reaction.

Cl⁻ + HI

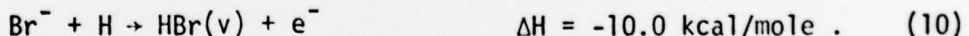
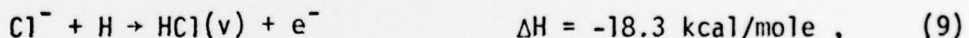
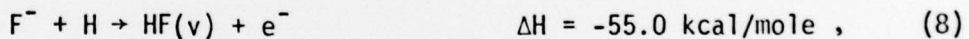
The rate constant for this reaction was determined to be $k = 4.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and iodide was found to be the only ionic reaction product. By using a variety of filters (for which transmission vs. wavelength was separately calibrated) and an HCl gas filter, we have determined that the

distribution of $v=2/v=1$ in HCl is 0.26/0.74. Experiments are presently underway to estimate the fraction of total exothermicity which goes into vibrational excitation; moreover infrared emission will be viewed at successive port windows to confirm the observation of initial vibrational distributions. We also plan to examine the effect of increased kinetic energy of chloride ion, imparted in the drift region, on the vibrational product state distribution.

These initial studies have already demonstrated the tremendous power and versatility of the infrared chemiluminescence flowing afterglow system. The opportunities for further research are enormous. We plan to study infrared emission from hydrogen fluoride and hydrogen bromide formed by proton abstraction reactions similar to eq. (2) and (3):



Associative detachment reactions forming the hydrogen halides will also be studied:



The generation of hydrogen halides by these energetically and mechanistically different routes will provide much interesting dynamical information.

Another source of vibrationally excited hydrogen halides is ion-ion recombination, an area of immense theoretical interest and practical importance in the atmosphere. For example, the rapid dissociative recombination of ammonium ion with chloride ion

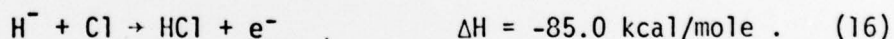
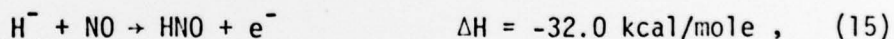
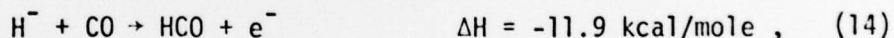


is extremely exothermic and should generate HCl and NH₃ in highly excited vibrational levels. Detection of these vibrational emissions using the infrared chemiluminescence flowing afterglow will represent the first direct detection of the products of an ion-ion recombination process. The large energy released in this reaction is especially intriguing since it will allow probing of the high vibrational levels inaccessible by neutral-neutral or ion-neutral processes.

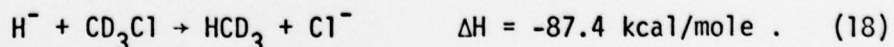
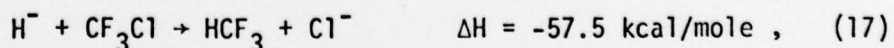
A number of reactions which produce NO⁺ in disturbed atmospheres, possibly in vibrationally excited states, will be an important area of study with our apparatus. For example, we will determine the extent of vibrational excitation and lifetimes of vibrationally excited NO⁺ produced by reactions such as:



A particularly interesting and versatile anion for infrared chemiluminescence studies is the hydride ion, H⁻. This species is involved in several intriguing associative detachment reactions:



The last reaction is related to the well studied associative detachment reaction of hydrogen atoms and halide ions (eq. 9). We have recently begun a study of the reaction of hydride ion with a pair of organic neutrals:



While these are rather simple chemical processes, they represent exceedingly complex dynamical problems. We seek to observe infrared chemiluminescence

from CHF_3 and CHD_3 . In both cases the newly formed bond is between carbon and hydrogen; the C-H frequency at 3000 cm^{-1} is well separated from the rest of the molecular vibrations. This fact and a number of other considerations indicate that we should be able to observe infrared emission before intra-mode vibrational scrambling sets in. These systems therefore represent an excellent starting point for a partial unravelling of the underlying dynamical framework of organic ion-molecule reactions. Preparatory to these experiments we have studied the means of H^- production in helium and argon buffer gases. The heavier buffer gas is essential for minimizing V-T processes in vibrationally excited polyatomic product molecules.

Publications:

V. M. Bierbaum, G. B. Ellison, J. H. Futrell, and S. R. Leone, "Vibrational Chemiluminescence from Ion-Molecule Reactions: $O^- + CO \rightarrow CO_2^+ + e^-$," J. Chem. Phys. 67, 2375 (1977).

T. S. Zwier, V. M. Bierbaum, G. B. Ellison, and S. R. Leone, "Vibrational Chemiluminescence and Product State Distributions of Ion-Molecule Reactions: $Cl^- + HBr, HI \rightarrow HCl(v) + Br^-, I^-$," to be submitted to J. Chem. Phys.

Figure Captions

- Figure 1. Schematic of flowing afterglow apparatus constructed for wavelength resolved infrared emission studies of ion-molecule reactions. Major modifications to detect infrared emission from vibrationally excited products of ion-molecule reactions include port windows, optimization for optical detection, ion modulation region (consisting of a fine mesh grid across the flow tube), ion drift region, and wavelength-resolved background limited infrared detector.
- Figure 2. Logarithm of chloride ion intensity (counts/second) versus flux of HX neutral reactant (SCCM). Helium pressure = 0.4 torr, helium flow = 10.4 SLPM, reaction length = 55 cm. For upper line, HX = HI and $k = 4.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For lower line, HX = HBr and $k = 7.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- Figure 3. Ion modulation signals:
- (a) Voltage pulse on grid, 0 to -10 V, applied to momentarily stop Cl^- ions.
 - (b) Pulsed modulation of HCl(v) infrared chemiluminescence as a result of the decreased Cl^- concentration.
 - (c) Pulsed modulation of Cl^- counts in mass spectrometer.
- The infrared signal and ion counts occur later in time because of the time required to traverse the flow tube. The infrared and ion signals show appreciably greater width due to axial diffusion of the ions to fill in the dip created by the pulsed modulation.
- Figure 4. Relative HCl infrared emission intensity versus flow of HBr (SCCM), demonstrating that the entire chemiluminescence signal is due to the ion-molecule reaction of $\text{Cl}^- + \text{HBr}$ since the signal limits with the proper rate constant for the ion-molecule reaction.

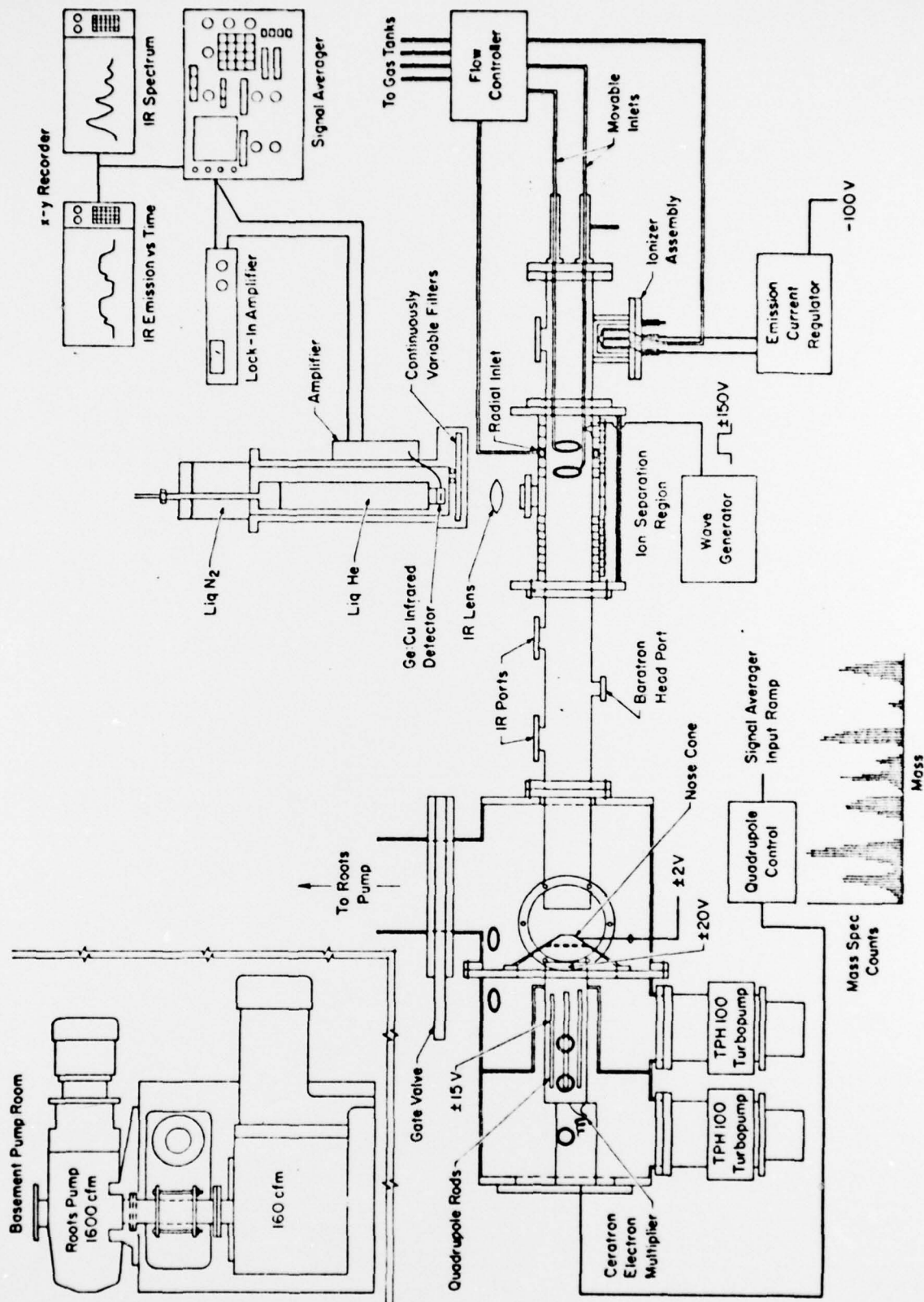


Fig. 1

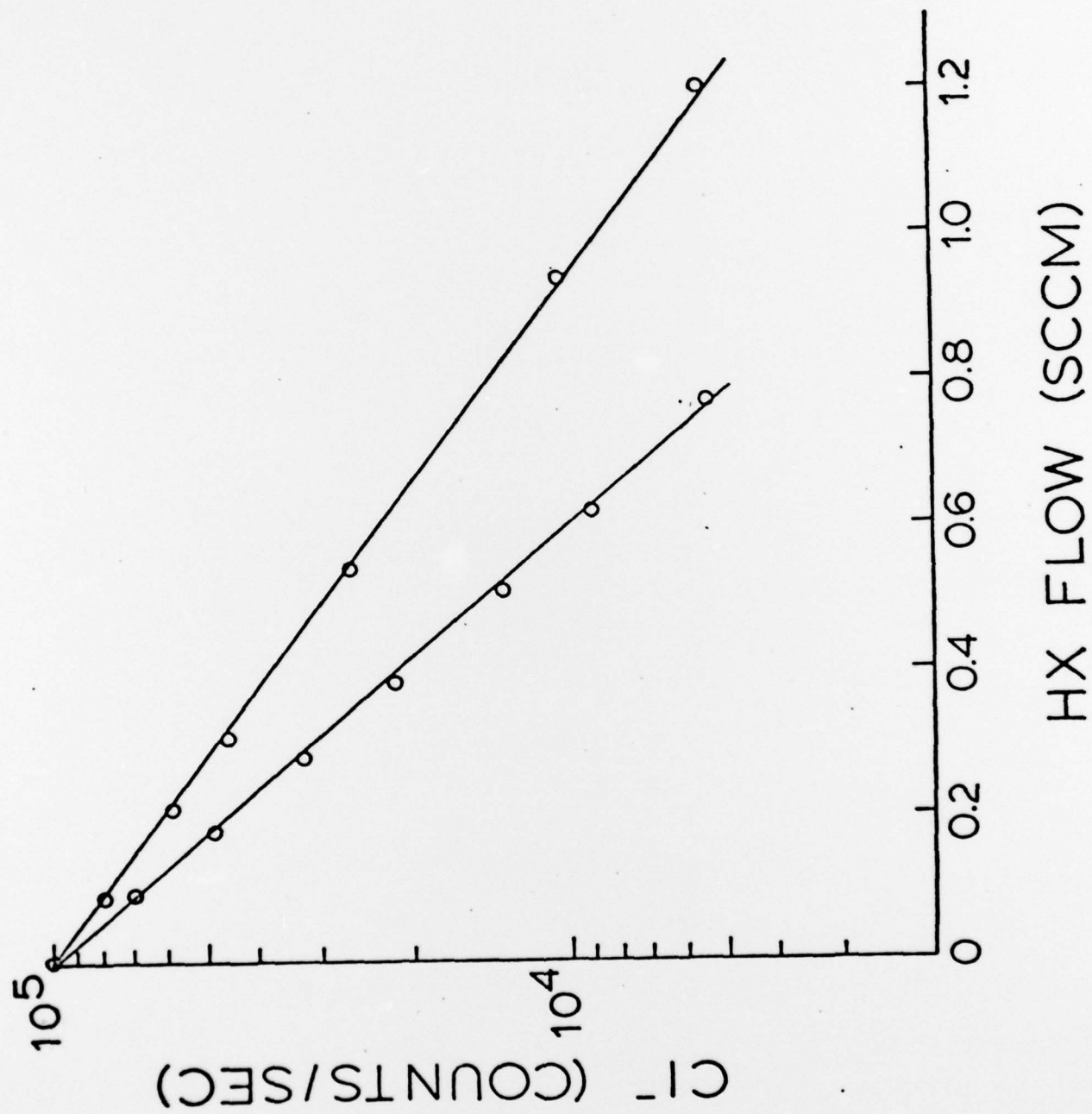


Fig. 2

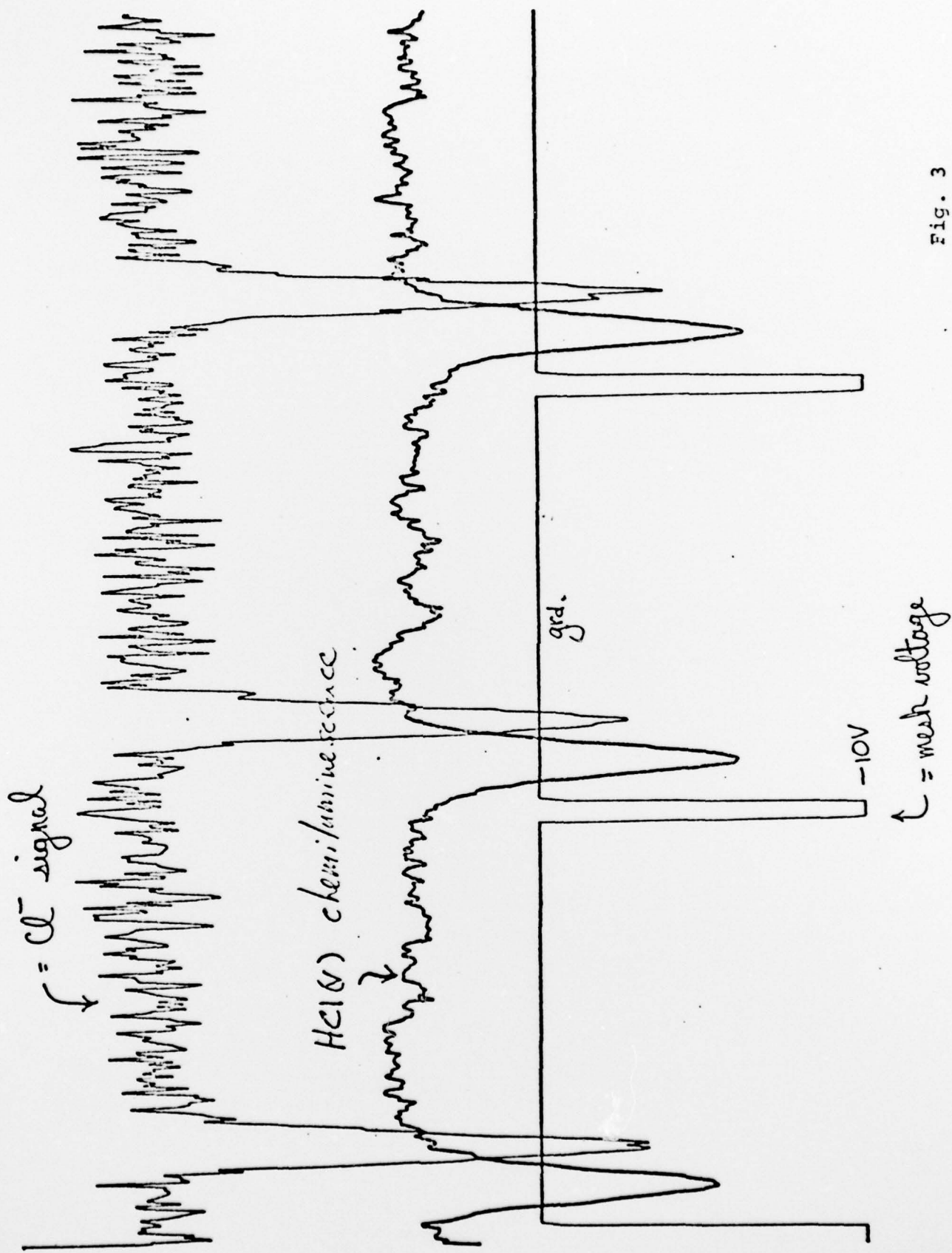


Fig. 3

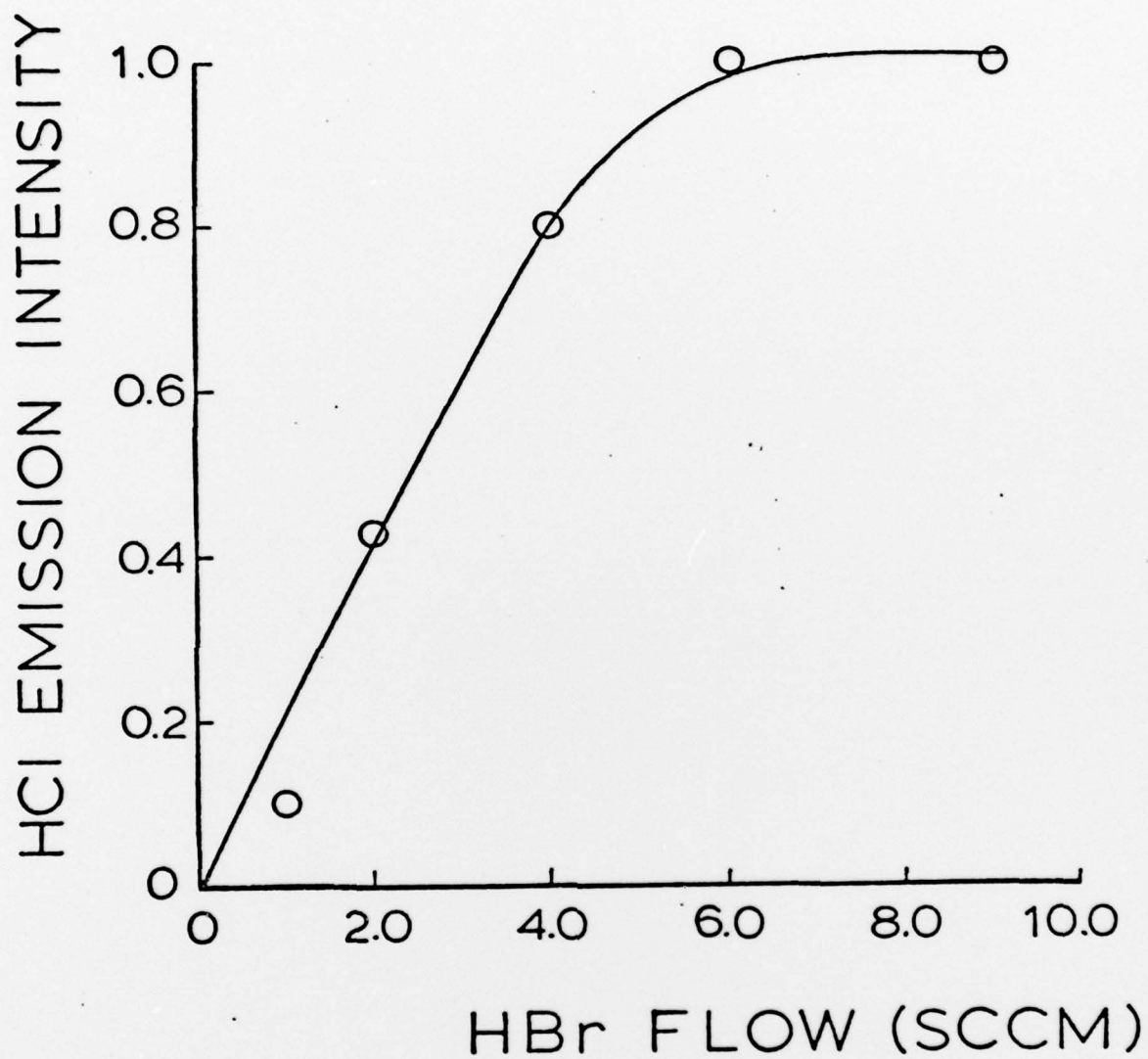


Fig. 4